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The Structure of Pb(II) Ion in Hyper-Alkaline Aqueous Solution

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Abstract

The structure of lead(II) in hyper-alkaline aqueous solutions has been determined by EXAFS and Raman spectroscopy, and from *ab initio* quantum chemical calculations. The formation of a single species was observed, in which the Pb-O bond distance is remarkably short, 2.216 Å, and the complex is non-linear. From single crystal X-ray data, the bond lengths for O-coordinated lead(II) complexes with low coordination numbers are spread over an unusually wide interval (*e.g.*, 2.216 – 2.464 Å for $N = 3$). The Pb-O bond distance is within the range of three coordinated complexes (*i.e.*, $[Pb(OH)_3]^-$ or $[PbO(OH)_2]^{2-}$) but the possibility of the two coordinated $[PbO(OH)]^-$ complex has also been considered. The observed Raman spectrum and that calculated for $[Pb(OH)_3]^-$ show obvious similarity. Predicted bond lengths are also consistent with the presence of $[Pb(OH)_3]^-$ and exclude the formation of Pb=O double bond(s). These observations together with experimentally established analogies between Pb(II) and Sn(II) in hyper-alkaline solutions suggest, that the last stepwise hydroxido complex of both tin(II) and lead(II) is $[M(OH)_3]^-$. The structure of the complexes is trigonal pyramid.

Introduction

The most common oxidation state of lead in nature is Pb(II). Because of its high toxicity,[1] the knowledge of hydrolytic equilibria of Pb(II) (both qualitative and quantitative terms) is of high relevance, both in the close-to-neutral pH-s of natural waters and living organisms[2], and in solutions of high pH-s, which are of industrial importance.[3] Upon hydrolysis in dilute aqueous solutions in the range of $2 < pH < 13$, lead(II) forms mononuclear complexes with the stoichiometry of $[Pb(OH)]^+$, $[Pb(OH)_2]^0$ and $[Pb(OH)_3]^-$.[4,5] Furthermore, at higher Pb(II)-concentrations, the formation of polynuclear complexes as $[Pb_3(OH)_4]^{2+}$, $[Pb_4(OH)_4]^{4+}$ and $[Pb_6O(OH)_6]^{4+}$ has been reported as well.[4,5]

Much controversy surrounds the composition of the Pb(II) complex(es) forming in hyper-alkaline aqueous solutions. The simplest speciation picture includes the exclusive formation of the $[Pb(OH)_3]^-$ even at the very alkaline end of the pH-scale and was supported by potentiometric,[6] polarographic,[7-9] and solubility[10,11] measurements. Ultracentrifuge[12] and light scattering[13] data were, however, interpreted in terms of the formation of $[Pb(OH)_4]^{2-}$ and from potentiometric titrations[15] using Pb/Hg electrode even the formation of the $[Pb(OH)_6]^{4-}$ species was suggested. In a recent work of Perera *et al.*[15] the formation of the Pb(II)-hydroxido complex with the stoichiometry of 1:4 was deduced, primarily from combined pH-spectrophotometric measurements. From Raman spectra, the formation of the two-coordinated complex, $[PbO_2]^{2-}$ was also suggested. However, the structure of the complex(es) formed in these hyper-alkaline conditions was not determined experimentally.

The main objective of the present work is to reveal the identity and structure of lead(II) complex(es) present in hyper-alkaline aqueous solutions. To achieve this, X-ray absorption spectroscopy (XAS) measurements have been carried out on solutions containing NaOH ($4\ M \le C_{NaOH} \le 16$ mol·dm^{-3}) and lead(II) (0.2 mol·dm^{-3}). The EXAFS measurements were supplemented with Raman spectroscopy and *ab initio* quantum chemical calculations.

Experimental section

Reagents and solutions

Analytical grade NaOH (ANALR NORMAPUR) was dissolved in distilled water with intensive stirring and cooling to prepare the alkaline stock solution. In this way ~50 % (w/w) NaOH solution is achievable; the concentration of the solution is ~19 mol·dm^{-3}. The concentration was calculated from the density of the solution, determined by a picnometer, according to literature procedures.[16] The carbonate content was minimized as described elsewhere.[17] The stock solution as well as the sample solutions were stored in caustic resistant Pyrex bottles with a tightly fitted screw-top.

The lead(II) stock solution, $C_{Pb(II)} = 1$ mol·dm^{-3} and $C_{HNO3} = 0.05$ mol·dm^{-3}, was prepared by dissolving analytical grade lead(II) nitrate, $Pb(NO_3)_2$ (Sigma Aldrich), in analytical grade nitric acid in order to avoid the hydrolysis of the lead(II) ions when diluted by distilled water. The caustic lead(II) solution was prepared by adding the calculated amount of the lead(II) stock solution drop-wise to the NaOH solution, in a small Pyrex bottle, for which a custom-made screw-top was fabricated with two small holes for the argon gas in- and outlet and a bigger one for the addition of the lead(II) stock solution. The calculated amount of the freshly prepared lead(II) stock solution was added drop-wise to 25 mL of the appropriately diluted NaOH solution with continuous and intense argon bubbling through the sample and stirring. The NaOH solutions were diluted by weight from the concentrated stock solution.

X-ray absorption measurements

The X-ray absorption spectra for lead were collected at the wiggler beam-line I811 at MAX-lab, Lund University, Sweden, using the MAX II storage ring operating at 1.5 GeV and a maximum current of 250 mA. The maximum flux on the sample is 5×10^{11} at 9 keV on a $(0.5\ mm)^2$ surface area. The

measurements were performed in fluorescence mode at the lead L_3-edge. The energy scales of the X-ray absorption spectra were calibrated by assigning the first inflection point of the lead L_3 edges of metallic lead foil to 13038.0 eV.[18] The samples were measured in cells were made of a 1.5 mm Teflon spacer and 6 μm polypropylene X-ray film hold together with titanium frames. The analysis of the data was performed with the EXAFSPAK[19] and FEFF[20] program packages allowing the determination the structure parameters of the local coordination around lead(II).

FT-Raman spectroscopy

Raman spectra were recorded on a BIO-RAD Digilab Division dedicated FT-Raman spectrometer equipped with liquid nitrogen cooled germanium detector and CaF_2 beamsplitter. The excitation line was provided by a Spectra Physics T10-106C Nd:YVO_4 laser at 1064 nm. The spectra were recorded between 3600 – 100 cm^{-1} with 4 cm^{-1} resolution. 4096 scans were collected for each spectrum. The excitation power was 280 mW at the sample position. The spectrometer was controlled by using BIO-RAD Win IR 3.3 software. The samples were placed in a 1 cm path length quartz cuvette. Spectra were recorded at room-temperature. Data were processed by SpekWin software and the fitting of the Lorentzian curves was performed with QtiPlot.

Computational methods

The complexes studied by computational methods included $[Pb(OH)_3]^-$, $[PbO(OH)]^-$, $[PbO_2]^{2-}$, $[PbO(OH)_2]^{2-}$ $Pb(OH)_2$ and $[Pb(H_2O)_3]^{2+}$. Optimizations and frequency analyses were performed using the GAUSSIAN 09 program with density functional theory (DFT) at the M052x/6-311++G** computational level. We systematically modeled solvent effects by representing H_2O as a polarizable continuum, according to the method implemented in the PCM-SCRF (self-consistent reaction field) procedure in the Gaussian program. We take into account some cases explicitly the hydration shell of these complexes, but the calculated properties do not change significantly compared to the PCM method, so we do not discuss those results.

Results and discussion

From extended X-ray absorption fine structure spectroscopy (EXAFS), bond lengths ($r_{Pb\text{-}O}$) can be more accurately determined than the corresponding coordination numbers (N).[21] The relationship between bond distance and coordination number may be extracted from single crystal X-ray data. Therefore in most cases (*i.e.,* for transition metal complexes) this relationship can be used to accurately estimate the coordination number from the observed bond distance.[22,23] The $r_{Pb\text{-}O}$ and N values of crystalline solid O-coordinated lead(II) compounds were collected from the Inorganic Crystal Structure Database and the Cambridge Crystal Structure Database[24,25], and were published in a previous paper[26] (except for those relating to complexes with $N = 3$ and the only one example for $N = 2$, shown in Table S1). The $r_{Pb\text{-}O}$ *vs.* N data collected are shown on Figure 1. The bond lengths for O-coordinated lead(II) complexes, in particular for those with low coordination numbers are spread over an unusually wide interval (*e.g.,* 2.216 – 2.464 Å for $N = 3$). This is most likely due to the stereo-chemical impact of the occupied anti-bonding orbitals of lead(II).

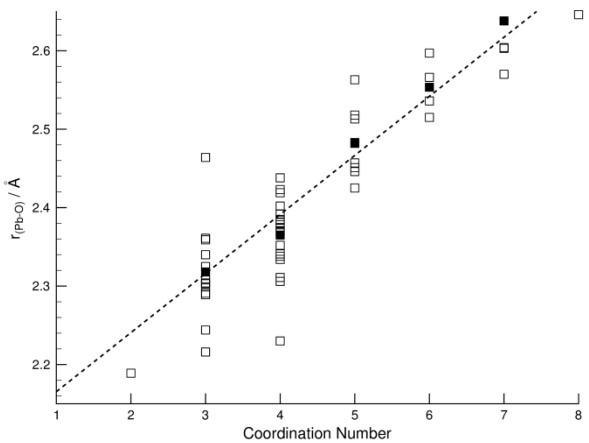

Fig. 1. Summary of mean bond distances in O-coordinated lead(II) compounds (details in Tables S1, and ref. 26), and the relationship between the mean Pb-O bond lengths and the coordination. The filled symbols stand for the average values. The dashed line represents the linear trend-line of the mean Pb-O bond distances as function of coordination number.

As the valence electron structure of lead(II) is analogous to that of tin(II), therefore the hydrolysis of lead(II) in highly alkaline media is expected to have some similarities with tin(II). Unfortunately, the solubility of Pb(II) in hyper-alkaline solutions was found to be insufficient to perform accurate H_2/Pt potentiometric measurements, similar to those done for Sn(II).[27] Therefore some structural conclusions are based on the similarity of Pb(II) and Sn(II). EXAFS measurements were carried out on aqueous samples containing 0.2 mol·dm^{-3} lead(II) in 4.0, 8.0 and 16.0 mol·dm^{-3} NaOH. The results are shown in Table 2. No change in the local structure around lead(II) was observed with changing hydroxide concentration, and there was only one kind of species detected (Figure 2). In this species, the Pb-O bond distance was determined to be 2.216 Å. It is indeed shorter than the average Pb-O bond distance for the three-coordinated lead(II) complexes with O-donor ligands, (2.318 Å, calculated as the average of 10 known structures). However, it is still within the interval of the observed bond distances. For lead(II), to the best of our knowledge, the structure of only one $N = 2$ O-coordinated complex has been reported so far (with $r_{Pb\text{-}O} = 2.189$ Å). The fitting of the experimental EXAFS data was carried out with holding the coordination number constant at a value of 3. However, similarly to that observed for analogous systems containing Sn(II),[27] good agreement between the observed and calculated data was achieved by assuming $N = 2$. On the other end, the case for $N = 4$ was discounted on the ground, that the experimentally obtained $r_{Pb\text{-}O} = 2.216$ Å is far out of the bond length interval obtained for solid complexes with $N = (2.30\text{-}2.46$ Å). Therefore, the formation of any kind of 4-coordinate Pb(II)-hydroxido complex, *e.g.,* $[Pb(OH)_4]^{2-}$, in our systems can be ruled out. Of the remaining structures, with $N = 3$ $[Pb(OH)_3]^-$ and $[PbO(OH)_2]^{2-}$, while with $N = 2$ $[PbO(OH)]^-$ and $[PbO_2]^{2-}$ can be considered.

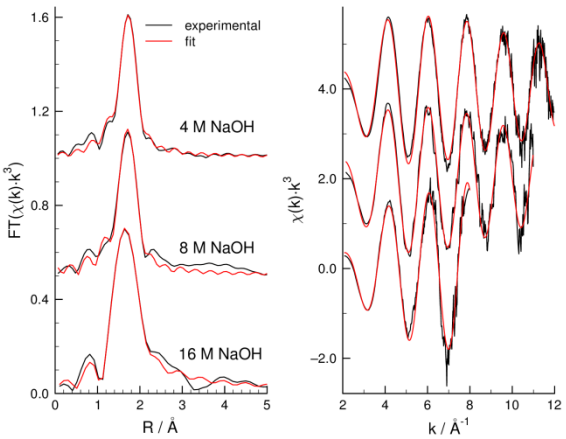

Fig. 2 The experimental and the fitted Fourier-transform of the k^3-weighted EXAFS data of the alkaline lead(II) samples: Pb20_4, Pb20_8 and Pb20_16 (A); the experimental and the fitted k^3-weighted EXAFS data, respectively (B).

Table 1 Composition of hyper-alkaline aqueous lead(II) samples studied expressed in total molar concentrations, and the structure parameters in the refinements of the EXAFS data collected at ambient room temperature using the EXAFSPAK program package including number of Sn-O bond distances, *N*, mean Sn-O bond distance, *r*/Å, and Debye-Waller factor coefficient, σ^2/Å^2, the threshold energy, E_o/eV, the amplitude reduction factor the goodness, S_o^2, the goodness of fit, *F*/%, as expressed in the EXAFSPAK program package, ref. 19.

***N*=3**	Pb20_4	Pb20_8	Pb20_16
C_{NaOH}	4	8	16
$C_{Pb(II)}$	0.20	0.20	0.20
r	2.216	2.222	2.216
σ^2	0.033	0.033	0.021
E_o	13064.0	13064.7	13065.0

Raman spectrum of a Pb(II) containing solution ($C_{Pb(NO3)2}$ = 0.1 M) with C_{NaOH} = 4.0 M has been recorded. A strong peak at ~424 cm^{-1} and a shoulder at ~355 cm^{-1} has been observed on the spectrum, both correspond to Pb-O symmetrical and antisymmetrical stretching vibrations. A strong signal due to the symmetric stretching mode of NO_3^- ion was also observed at 1048 cm^{-1}. The Raman spectrum of a solution with similar composition to ours was published in ref. 15, and a peak at 419 cm^{-1} with a shoulder at 377 cm^{-1} was reported. These values are in good agreement with those obtained by us. In ref. 15 the sample has been prepared from PbO(s) and a signal at 1064 cm^{-1} has also been reported and was assigned to the species $[PbO_2]^{2-}$. It is important to note, that there are obvious similarities between the Raman spectra of hyper-alkaline solutions containing Sn(II) and Pb(II). In the former, a strong peak was found at ~430 cm^{-1} and a weak at ~490 cm^{-1}, and were assigned to the species $[Sn(OH)_3]^-$.[27]

Quantum mechanical calculations were performed to obtain proposed bond lengths and Raman band positions for the complexes with structures shown in Figure 3 and the results of these calculations are summarized in Table 2.

Fig. 3 Ball and stick models for the oxido-hydroxido complexes of Pb(II) studied.

Table 2. Comparison of the experimentally found and calculated bond lengths and Raman band positions for various hypothetic oxido-hydroxido complexes of Pb(II).

	N	r_{Pb-O}[a] **(Å)**	$r_{Pb=O}$[b] **(Å)**	Raman peaks **(cm^{-1})**
Experimental	-	2.216		355w, 424s[c] (377w, 419sd[d])
$[Pb(OH)_3]^-$	3	2.232	-	370s, 413s
$[PbO(OH)_2]^{2-}$	3	2.430	2.050	222w, 256w, 523s
$[PbO(OH)]^-$	2	2.256	1.990	363w, 603s
$[PbO_2]^{2-}$	2	-	2.103	203w,452s,496s
$Pb(OH)_2$	2	2.123	-	459w, 488s
$[Pb(H_2O)_3]^{2+}$	3	2.440	-	261w, 291w

w: weak; s: strong;[a] Pb−O single bond; [b] Pb=O double bond; [c] current work; [d] data taken from ref. 15

As expected, the calculated bond lengths for Pb−O single bonds are significantly longer (2.23-2.43 Å), than those of Pb=O double bonds (1.99-2.10 Å) and the calculated bond lengths are for single bonds very close to that obtained experimentally. On this ground, the formation of the fully dehydrated species $[PbO_2]^{2-}$ can be ruled out. If there were a mixed oxido-hydroxido complex, the two different bond lengths would be present in one species. Since the exchange of the H^+ between the two oxygen atoms is slow comparing to the EXAFS timescale, therefore two distinct peaks should be seen in case of $[PbO(OH)]^-$, which is obviously not the case (see Fig. 2 (A) and Table 1). On that ground $[PbO(OH)_2]^{2-}$ and $[PbO(OH)]^-$ can be discounted and only the $[Pb(OH)_3]^-$ remains.

The observed and calculated Raman spectra (Table 2) also support the exclusive formation of $[Pb(OH)_3]^-$. The calculated Raman peak positions for this species almost perfectly match with those obtained by us and observed in previous studies. On the other hand, those for the other species show no resemblance to the observed one.

Conclusions

In summary, EXAFS spectroscopic measurements show that only one kind of lead(II) complex is present in strongly alkaline aqueous solutions, containing 4.0-16.0 mol·dm^{-3} NaOH. The predominating complex is the mononuclear $[Pb(OH)_3]^-$ with short Pb-O bond length, 2.216 Å. This is just within the range of bond distances observed for three-coordinate lead(II) complexes. The agreement between the calculated Raman spectrum of $[Pb(OH)_3]^-$ and the experimentally observed one fully supports the exclusive (or at least predominant) presence of this mononuclear complex in these hyper-alkaline aqueous solutions.

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† Electronic Supplementary Information (ESI) available: bond lengths and angles found for N = 3 and 2 O-coordinated Pb(II) complexes.. See DOI: 10.1039/b000000x/

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Electronic Supplementary Information

Table S1 The oxygen coordinated lead(II) structures used for determine the coordination number – Pb-O distance relationship for coordination number = 2, 3, 4, 5, 6, 8. The list is based on the data collected from the Inorganic Crystal Structure Database (ICSD) and the Cambridge Structural Database (CSD); *N* = coordination number; references marked in red text are omitted from the mean bond distance and angle. All the other structural data are listed in reference 4.

N	CSD code	$d_{Pb\text{-}O}$	∠O-Pb-O	Reference
2	VEYKUH	2.189 Å	100.6 ^{o}	Rekken, B. D.; Brown, T. M.; Olmstead, M. M.; Fettinger, J. C.; Power, P. P. *Inorg. Chem.* **2013**, *52*, 3054.
	Mean	**2.189 Å/1**		
3	QAHVOL	2.216 Å	86.5 ^{o}	Nehete, U. N.; Chandrasekhar, V.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Organometallics* **2004**, *23*, 5372-5374.
3	QEXVUL	2.244 Å	77.7 ^{o}	Abakumov, G. A.; Cherkasov, V. K.; Piskunov, A.V.; Lado, A. V.; Fukin, G. K; Abakumova, L. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **2006**, 1103-1111.
3	OLAZAD	2.289 Å	82.9 ^{o}	Mauck, C. M.; van den Heuvel, T. W. P.; Hull, M. M.; Zeller, M.; Oertel, C. M. *Inorg. Chem.* **2010**, *49*, 10736-10743.
3	NIPKAY	2.291 Å	78.3 ^{o}	Parr, J.; Ross, A. T.; Slawin, A. M. Z. *Polyhedron* **1997**, *16*, 2765-2770.
3	MAJGOT	2.299 Å	83.2 ^{o}	van Zandt, W.; Huffman, J. C.; Stewart, J. L. *Main Group Met. Chem.* **1998**, *21*, 237-240.
3	MUKYIA	2.303 Å	77.1 ^{o}	Yu-Jun Shi; Yan Xu; Xue-Tai Chen; Ziling Xue; Xiao-Zeng You *Eur. J. Inorg. Chem.* **2002**, 3210-3213.
3	QEXVUL	2.304 Å	83.9 ^{o}	Abakumov, G. A.; Cherkasov, V. K.; Piskunov, A.V.; Lado, A. V.; Fukin, G. K; Abakumova, L. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **2006**, 1103-1111.
3	QEKZAI	2.308 Å	78.5 ^{o}	Oldag, T.; Keller, H.-L. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1267-1272.
3	MAJGOT	2.325 Å	84.5 ^{o}	van Zandt, W.; Huffman, J. C.; Stewart, J. L. *Main Group Met. Chem.* **1998**, *21*, 237-240.
3	NIPJUR	2.340 Å	75.1 ^{o}	Parr, J.; Ross, A. T.; Slawin, A. M. Z. *Polyhedron* **1997**, *16*, 2765-2770.
3	NIPJOL	2.359 Å	78.4 ^{o}	Parr, J.; Ross, A. T.; Slawin, A. M. Z. *Polyhedron* **1997**, *16*, 2765-2770.
3	QEKYUB01	2.361 Å	77.5 ^{o}	Oldag, T.; Keller, H.-L. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1267-1272.
3	BIBTIQ	2.464 Å	81.9 ^{o}	Naumov, P.; Cakir, S.; Bulut, I.; Bicer, E.; Cakir, O.; Jovanovski, G.; Ibrahim, A. R.; Usman, A.; Fun, H.-K.; Chantrapromma, S.; Ng, S. W. *Main Group Met. Chem.* **2002**, *25*, 175-176.
	Average	**2.318 Å**	**79.9 ^{o}/10 structures**	